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The Thermal Behavior Of Illinois Coal.

THE THERMAL BEHAVIOR OF ILLINOIS COALS IN THE LOW TEMPERATURE CARBONIZATION PROCESS

BY

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B. S., College of the City of New York, 1917

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THE GRADUATE SCHOOL

June 4, 1921

I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY SUPERVISION BY Benjamin Raczkowski Harris

ENTITLED "The Thermal Behavior of Illinois Coals in the Low Temperature Carbonization Process"

BE ACCEPTED AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE DEGREE OF Master of Science in Chemistry

S.

In Charge of Thesis

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*Required for doctor's degree but not for master's

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The problem was initiated by Professor S. W. Parr. I am greatly indebted to him not only for criticism and guidance but even more for the many ingenious instruments which he has devised, especially the adiabatic calorimeter, without which the investigation could not have been possible.

Thanks are due to Mr. C. E. Hollister, the department mechanician, who made all the special apparatus and originated many of its features and to Mr. Paul Anders who blew the glass apparatus.

Finally, I take pleasure in expressing my appreciation for valuable assistance, in the manipulation of apparatus, rendered by Messrs. J. M. Lindgren, H. D. Carter, F. B. Hobart and others.

It goes without saying, that I deeply feel my obligation to the great host of painstaking and devoted workers who have gone before, who have laid the cornerstones and erected the structure of our exact sciences. In particular, to that inspired sage and seer, Michael Faraday, I humbly bow my head in reverence and gratitude!

In this spirit, I offer the modest tract which follows.

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SECTION 1

INTRODUCTION

The fact that coal undergoes thermal decomposition essentially with evolution of heat has been for some time well known to chemists and coal technologists. Though the magnitude of this quantity of heat has been the subject of considerable speculation and research, there is still much to be desired as regards the reliability of the data available.

For a comprehensive history of the problem, the reader is referred to an admirable paper by Hollings and Cobb[1], since only such reference will be made to individual workers as will be necessary for the intelligent consideration of the questions treated below.

Included herewith, (SEE APPENDIX), is a table, rather complete it is hoped, of values to be found in the literature, for though Hollings and Cobb do give an exhaustive discussion of past investigations, they have not assembled into a compact form the various figures that are on record. It will suffice at this point to say that the exothermic heat values, thus far reported, vary between 1 and 7% of the calorific value of the coal, the variations being due both to the compositions of the coals and the methods employed. Further, such work as has been done since 1914, the date of the Hollings and Cobb publication, will be mentioned so as to bring the history up to date.

In a paper, misleadingly entitled, "A Comparative Method of Determining the Heat of Carbonization of Coal,"[2] exothermicity is discussed but the paper can in no sense be considered as contributing to our knowledge of the exothermic decomposition of

coal. The destructive distillation of lignin, prepared from spruce wood sawdust, has been recently described.[3] The reaction is distinctly exothermic as in the case of wood and cellulose. Ten to 15% of the calorific value is the magnitude assigned to the exothermic heat of wood in "Fuel Production and Utilization" (1920).[4] A patent,[5] recently granted to O. F. Stafford, claims the utilization of the exothermic heat as a feature of the process. To these may be added two investigations not covered by Hollings and Cobb, one before and one after their publication. Exothermicity was observed by Parr and Francis[6] in connection with another investigation and studied at some length by E. B. Vliet (unpublished reports, University of Illinois, 1917 and 1918).[7]

Of peculiar significance is the determination of this exothermic heat for the low temperature carbonization process developed at the University of Illinois, depending as it does on the autogenous heating of the coal being carbonized; namely, the coal is brought up to a suitable temperature when it furnishes its own heat exothermically, the whole mass being heated gently and uniformly, without the violent superheating of and consequent decomposition of products by the walls of the retort or oven.

SECTION 2

CRITICAL DISCUSSION OF THE AVAILABLE METHODS

The methods for the measurement of the exothermic heat of decomposition of coal that are available or, to be more accurate, the methods that have so far been used may be conveniently divided into four types. The names are arbitrary, serving merely for the purpose of differentiation:

1. Temperature rise method
2. Method of heat balances
3. "Heat loss" method
4. Direct measurement

The first was apparently originated by Hollings and Cobb. A crucible containing the coal to be tested and another similar crucible filled with a thermally inert substance, e.g. coke, are placed side by side in an electrical tube furnace. A thermocouple dips into each crucible and the thermocouples are connected in opposition. The furnace is then slowly and steadily heated, an inert atmosphere being maintained in the tube and readings are taken on the differential pyrometer. When these are plotted against actual temperatures of the coke, curves are obtained which indicate the thermal behavior of the coal at various stages of its decomposition. Essentially the same method, but with some modifications, was used by E. B. Vliet (unpublished report, University of Illinois, 1918). The results are purely qualitative and serve merely to show the zones of exothermicity, endothermicity and thermal neutrality, with only a very crude indication of the relative intensities.

The second method pretends to be quantitative and utilizes data

obtained from large scale industrial carbonization. A balance is struck between (1) the heat furnished to the retort or oven--by the fuel burned to effect carbonization--and (2) the heat yielded up by the retort, taking account of the sensible heat of ashes and coke, heat lost from setting by convection and radiation, heat carried out by flue gases and gases of decomposition, etc. The difference thus arrived at--the second quantity being greater than the first--is the heat given up by the coal during its decomposition. Euchene[8] and Barnum[9] are the principal contributors in this field. The method is obviously only very crudely quantitative, since many of the items considered are estimations of an unknown degree of accuracy.

The third method, which has by far yielded the most and probably also the best information has been worked with chiefly by Mahler,[10] Constam and Schlapfer,[11] Constam and Kolbe[12] and S. W. Parr and T. E. Layng (unpublished researches, University of Illinois). The combined calorific value of gas, tar, pitch and coke subtracted from the calorific value of the coal, from which they are obtained, gives a difference which is the "heat loss," i.e., the heat liberated by the coal while it is being carbonized.

It should be borne in mind, that in these quantitative methods, as well as in the method employed in the present investigation, to be described below, all determinations are made at room temperature and to arrive at the exothermic heat actually delivered at the more or less elevated temperature of decomposition, a calculation would have to be made according to Kirchoff's Law, taking into account the specific heats of the reactants and resultants.

Manifestly, such a calculation would be extremely difficult, if not impossible, the determination of the various specific heats, let alone their variation with temperature, being a feat in itself.

The direct measurement method was submitted to a brief test by E. B. Vliet, (unpublished report, University of Illinois, 1917) and abandoned as unfeasible. It consists in coking a weighed mass of coal in an inert atmosphere inside a calorimeter. Heat is supplied to the coal electrically and accurately measured; this constitutes the energy input. The energy output is obtained from the temperature rise and the water equivalent of the calorimeter system. The amount by which the energy output exceeds the energy input must obviously come from the coal and represents the exothermic heat. The water equivalent of the system is obtained in the same way, coke being used instead of coal. In this case, of course, there is no difference to be considered, the electrical energy input, converted to calories is divided by the temperature rise; the result is the water equivalent.

The weak point of the method is that the final result is a small difference between two large quantities, the accuracy necessarily suffering thereby. To put it another way, the quantity sought is in great danger of being "swamped" by the quantities actually measured. A typical case will serve to bring out this point. Under the conditions which obtained in the apparatus used in this investigation, an input of approximately 35,000 calories was required to raise the coal to 500° C and keep it there two minutes. The input was measured electrically (SEE SECTIONS 3 and 4 BELOW) with a probable accuracy of $\pm \frac{1}{2}\%$, so that the 35,000 was correct to $\pm$175 calories. The output, with a moderately exothermic coal, in such a case, would

be about 35,700 calories, measured by the temperature rise of the calorimeter system with an accuracy not worse than $\pm\frac{1}{2}\%$. The difference is 700 calories, correct to $\pm$175 calories and its percentage accuracy is only $\pm$25%. However, the only other quantitative method, is in a measure open to the same criticism, the heat of combustion of the coal and its carbonization products being large quantities and the difference relatively small. Moreover, it involves errors of collecting, sampling and analyzing of the gas, tar, pitch, and coke, something which is avoided in the direct measurement method. Further, too much emphasis cannot be laid upon the fact that the water equivalent is more than merely a water equivalent, it is at the same time a control of the most desirable type, a better than which could not be wished for. Various errors to which the determination would otherwise be subject are eliminated by the water equivalent determination being an exactly parallel experiment to the actual test, practically the only difference being that coal is replaced by a corresponding quantity of thermally inert coke. Just one such error will be considered in detail to show how it is removed by the feature above referred to. SECTION 3, below, will make it appear that the wires that carry the current to the "GRID" which heats the coal, might conceivably carry heat out of the calorimeter water into the air, thereby diminishing the energy output and decreasing the exothermic value. To be sure the wires were made 5 to 6 feet long so as to afford sufficient contact with the water before emerging into the air, but still there might be some heat leakage. Granting this to be the case--the leakage would at all events be small--the significant point to note is that it would be about the

same as in the water equivalent run; the same, in so far as the current, time of passage of current and temperature gradient between the "GRID" and air were the same. The two sets of conditions did correspond very closely in most cases. Now, a careful consideration of the relationships prevailing will show that under the conditions specified, such an error and numerous other errors, are absorbed by the water equivalent.

Minor errors not eliminated by the water equivalent are heats of solution of NH_3 and H_2S and other water soluble products of carbonization, escape of heat with gases of carbonization, etc.

A limitation of the apparatus used, though not of the method, was that it was not capable of treating coal at temperatures much above 500°C.

SECTION 3

DESIGN AND ARRANGEMENT OF APPARATUS

NOTE: Parts have been numbered in rotation but any one member bears the same number wherever it appears in the PLATES. Arabic numbers with Roman numerals as exponents, referring to the PLATES, will serve to locate the parts under discussion.

The leading objective in designing the apparatus proper for the decomposition of the coal was economy of heat input so as to render the ratio of exothermic heat to input as large as possible since it is that relation which in a large measure controls the accuracy (SEE SECTION 2). In this connection, three factors were of primary importance: first, low thermal capacity of the heating element, i.e., a minimum of material to heat up with the coal, second, good contact between the heating element and the coal and third, a minimum amount of radiation and conduction of heat to parts of the system other than those which it was desired to heat, which in turn depended upon insulation and duration of heating. However, effective insulation rendered the attainment of thermal equilibrium in the system, at the start of an experiment, extremely difficult. So that a compromise had to be struck between these two desiderata.

After considerable trial and tribulation the "GRID," PLATES I and VII, was evolved. A slab of soft "Alberene" stone was hacksawed to the shape indicated and 25 slots, 0.008 to 0.009 of an inch wide, were cut into the ends with a circular metal slitting saw. The stone teeth so formed were broken out at one end,

(background of PLATE I) and replaced when the ribbon was in position so as to allow the ribbon to expand, when heated, longitudinally rather than laterally which caused shorting. The actual heating was effected by approximately 95" of chromel ribbon $\frac{1}{4}$" wide and 0.005" thick, resistance per foot 0.442ohms, bent as shown and crimped in the middle of each bend so as to lend sufficient rigidity. The brass binding posts 70^{I} and 71^{I}, were slotted with a fine hacksaw, the ends of the ribbon slipped in, the whole drilled through brass and chromel and secured with a copper rivet. One of the grids made had a total resistance of 3.22 ohms, another 3.32 ohms. An Alberene stone plate, (not shown), 3 3/8" x 3 3/8" x 3/32" with a hole in the center to admit the thermocouple tube, $41^{III,IV}$ and two diagonally opposite corners cut out to make room for the binding posts 70^{I},71^{I} , was used for covering the grid to prevent the powdered coal from blowing out and to keep in the heat.

The grid was used in conjunction with the decomposition apparatus shown in PLATE II, disassembled in PLATE III, cross-section in PLATE IV, and hereinafter referred to for the sake of brevity as the "CARBONIZER." Elaborations were introduced as the necessity for them arose and space will not be taken to justify them indidually:

The carbonizer may well be looked upon as consisting of two parts, the upper and lower halves, held together by six clamps 63^{II}, 64^{II}, etc., the junction being rendered gas-tight by the gasket 72^{II}, cut out of sheet rubber 0.025" thick, The upper half carries:

1. the copper spiral tube, 67^{II}, through which gases

pass after the quenching of the grid (SEE SECTION 4).

2. the hard rubber member 65 II, VI which supports the binding posts 52II ,53 II of the thermocouple, 73VI and 50II, 51II of the leads 48II,III, 49II,III which carry the heating current to the grid.

3. the collar 76II,VI, which can be adjusted along the tube 66II,VI by means of the set screw 69II. The collar 76II engages the arms 57II, 58II and 59II which hold the carbonizer in position in the calorimeter can (not shown), a copper can 9" x 7" provided with 3 members soldered on its inside on which the projecting ends, of the arms 57II, 58II and 59II, rest. The arms 57 and 58 were cut in two so that the carbonizer might fit into the museum jar 1IV for evacuation and replacement of its atmosphere with nitrogen. When in use, the severed halves of the arms were held in place by the glass tubes 55II and 56II. Attention should also be called to the copper-constantan thermocouple 73VI and its "Pyrex" protecting tube 41III,VI, which is embedded in the coal between two ribbons when the apparatus is completely assembled. 75III,VI is a special nut which fixes the brass tube 66II,VI firmly on to the principal member of the upper half of the carbonizer. With the exception of numbers 54II, 60II, 61II and 62 II, which will be covered in SECTION 4, this completes the description of the upper half of the carbonizer.

The lower half of the carbonizer carries on the outside:

1. the rubber tube 46II,III for admitting nitrogen.

2. the #16B. and S. copper wire leads $49^{II,III}$ and $48^{II,III}$ which enter at 47^{III} and $47a^{III}$ respectively, and

3. the tube $68^{II,III,VI}$ (provided with the 30 mesh copper gauze 74^{VI}) for the escape of gases of decomposition.

On the interior, the lower half of the carbonizer, presents three "TRANSITE" pegs, (only two of which are shown $42^{III,VI}$ and $44^{III,VI}$), on which the grid rests. In addition to the pegs, there are two flexible cables, each about $1\frac{1}{4}$" long, (only one is shown, 43^{III}), the function of which is to complete the circuit between the binding posts 70^{I} and 71^{I} and the terminals of the leads 48^{III} 49^{III}, on the interior of the carbonizer.

PLATES VI and VII show a few additional features and the actual dimensions. In PLATE VI the two halves of the carbonizer are separated and the coil 67^{II}, the leads 48^{II}, 49^{II} and the arms 57^{II} 58^{II} 59^{II} are not shown for the sake of simplifying the drawing. PLATE VIII is a detail, self-explanatory, of the member $47^{II,III}$, ($47a^{III}$ is similar to it), and shows the manner in which the leads $48^{II,III}$ and $49^{II,III}$ enter the lower half of the carbonizer.

PLATES IV and V still remain to be described. The former is a photograph of the complete set-up, ready for a run; the latter, a diagrammatic representation of the electrical circuits. The storage batteries shown in IV were originally used but later abandoned in favor of 45 or 50 volts taken off the 110 D.C. circuit, $35^{IV,V}$. 10^{IV} is a Parr Adiabatic Calorimeter, manufactured by the Standard Calorimeter Co., Moline, Ill.; 33^{IV}, the water heater for the calorimeter. 6^{IV}, 7^{IV} Fahrenheit thermometers with a 65 to 90° range, calibrated at the Bureau of Standards, (Beckman thermometers of a

sufficiently large range were not available).

11^{IV} and 12^{IV}, and a third not shown, are pyrogallol wash-bottles for the purification of the Linde compressed nitrogen used for displacing the air in the carbonizer. 4^{II} is a reservoir for nitrogen and 5^{IV}a leveling bottle corresponding to it; 2^{IV} a drying tower intermediate between 4^{IV} and 1^{IV}, the museum jar in which the carbonizer was placed for evacuation. 9^{IV} a Dewar flask cold junction for the thermocouple 73^{VI}; 8^{IV}, a Siemens-Halske millivoltmeter used in connection with 73^{VI}. The coulometer $31^{IV,V}$ (SEE SECTION 4) is a glass jar 8½" x 2" containing: (1) 2 nickel gauze electrodes, (6 3/4" x 1 3/4", each provided with a copper wire lead, riveted on), (2) about 230cc. of 15% NaOH solution, prepared from chlorine-free NaOH and (3) about 15cc. of carefully purified mineral oil (boiling between 180 and 220° C) to prevent frothing. The coulometer is tightly sealed with a rubber stopper fitted with (1) the dropping funnel 32^{IV}, for the introduction of water and (2) a delivery tube (not distinctly shown) which is in communication with the gasholders 27^{IV} and 29^{IV}, of which 28 and 30 are the leveling bottles, and (3) the leads to the gauze electrodes. The two-way stop-cock $27a^{IV}$ permits 27 to be connected with either 31 and 29 or 17^{IV}, a water jacketed 200 cc. measuring burette, for which 18^{IV} is the leveling tube.

Other features of PLATE IV will be referred to in SECTION 4.

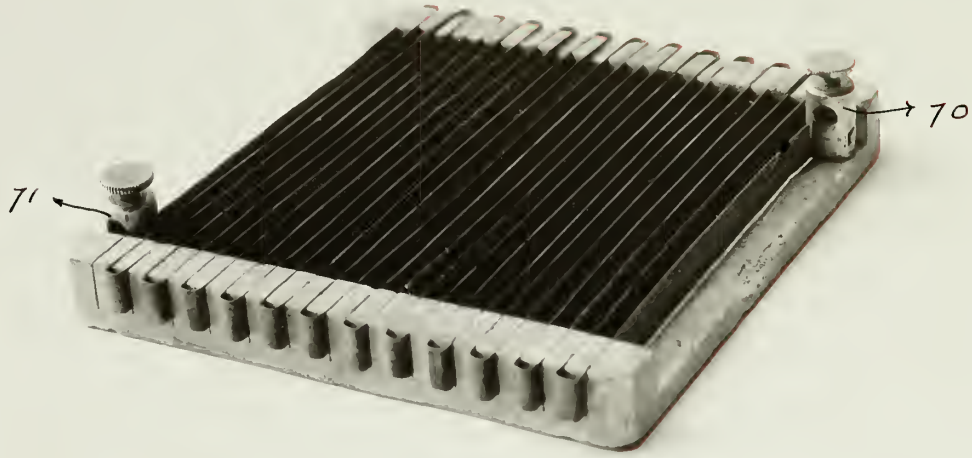

PLATE I

"GRID"

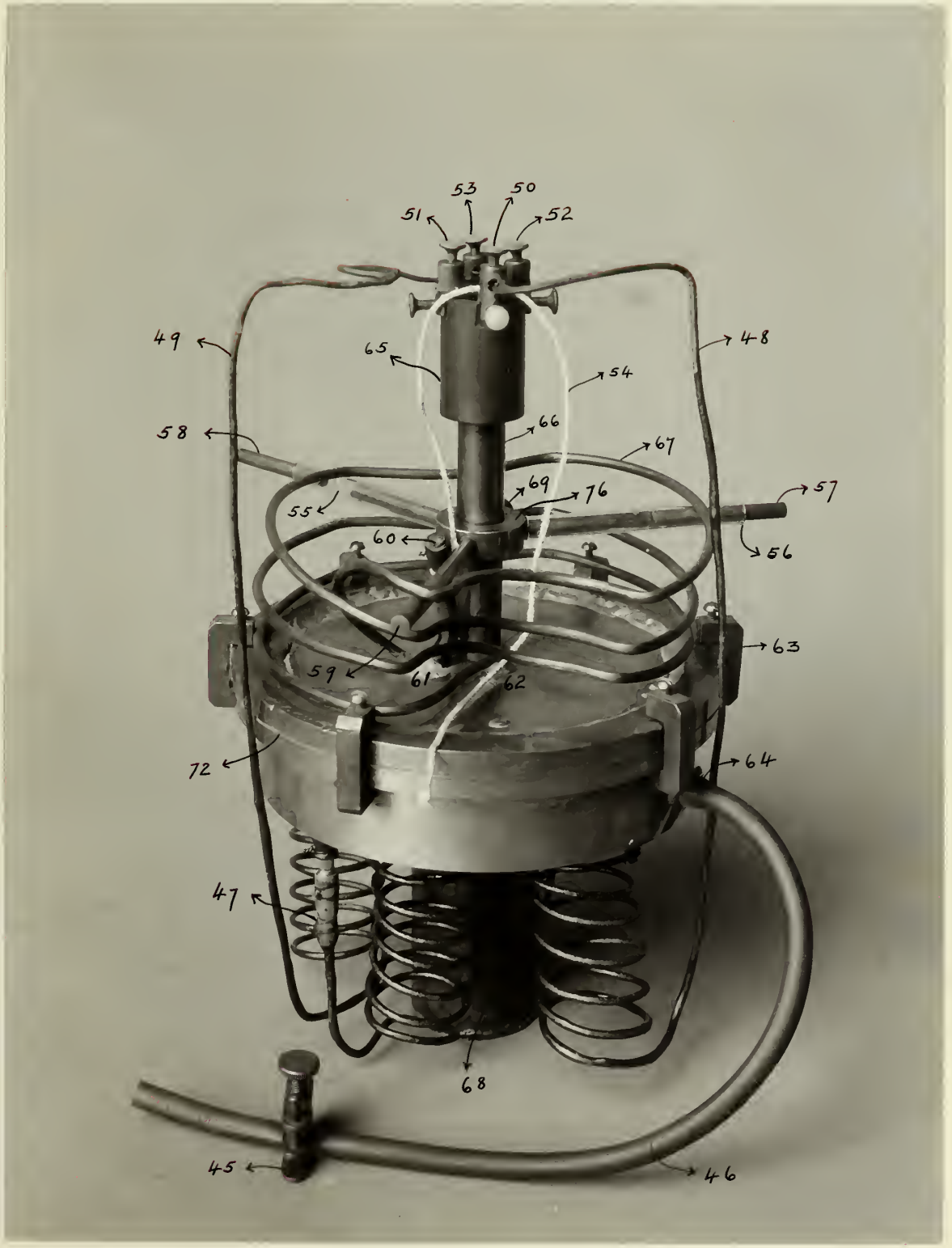
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PLATE II

PLATE III

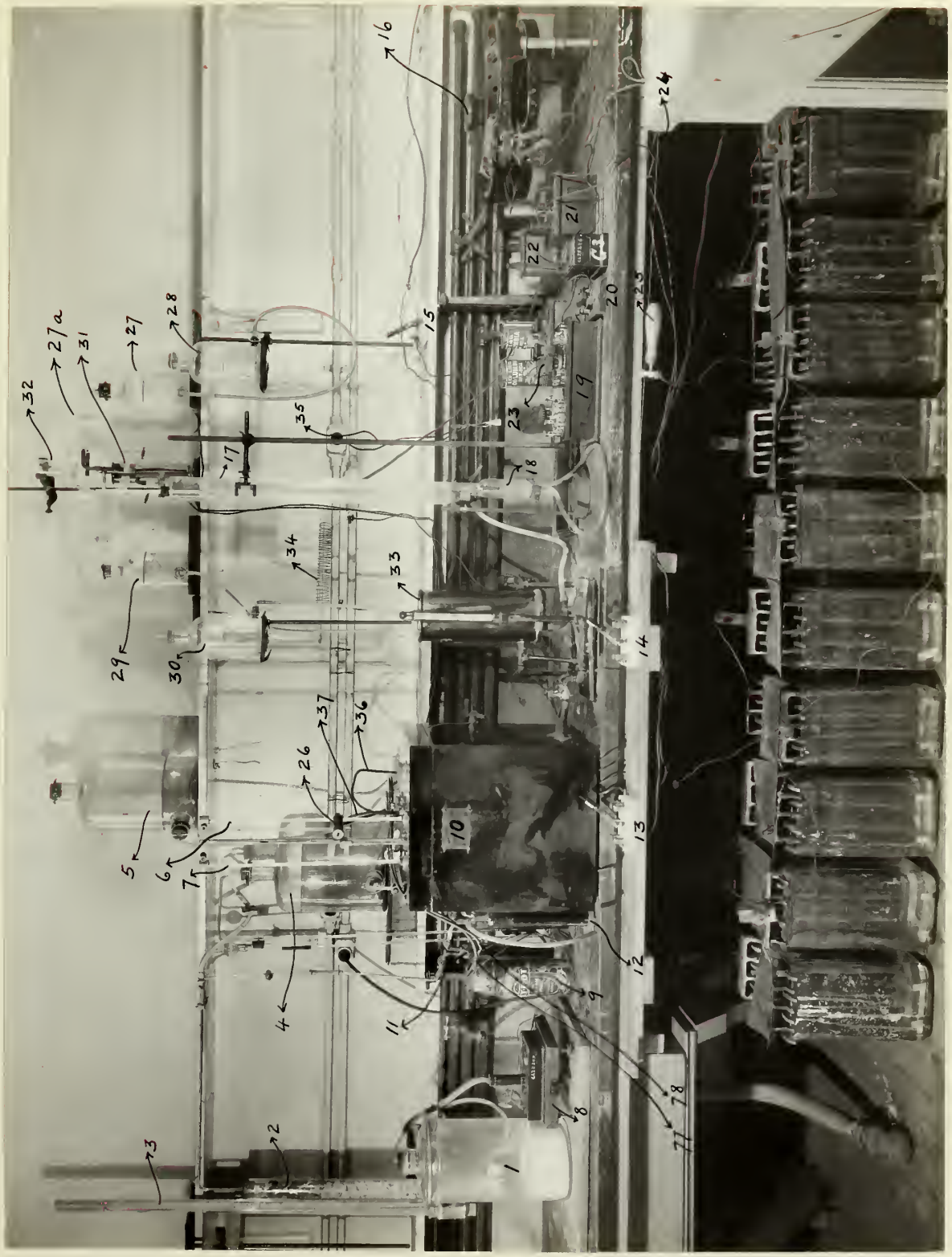
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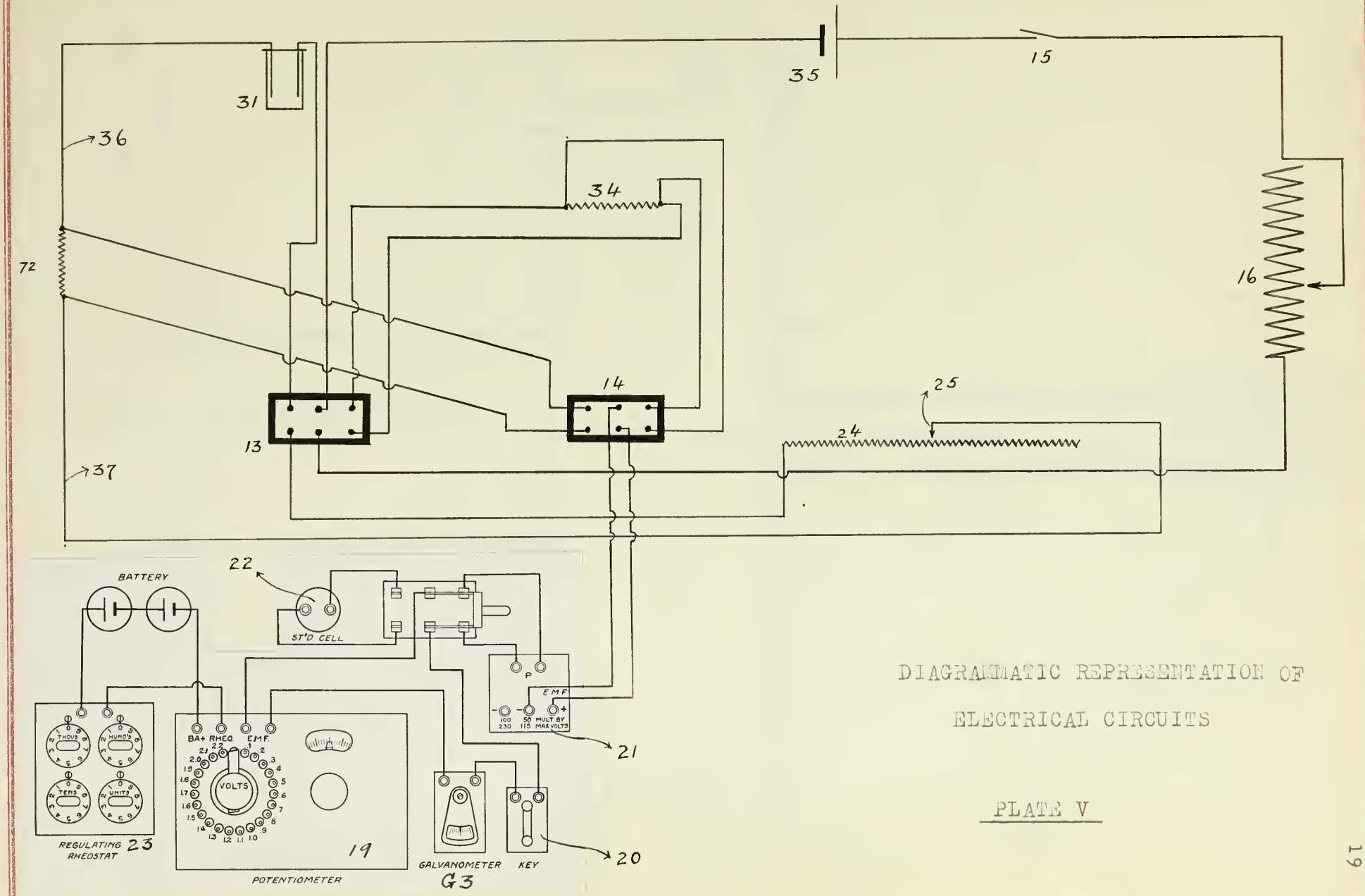
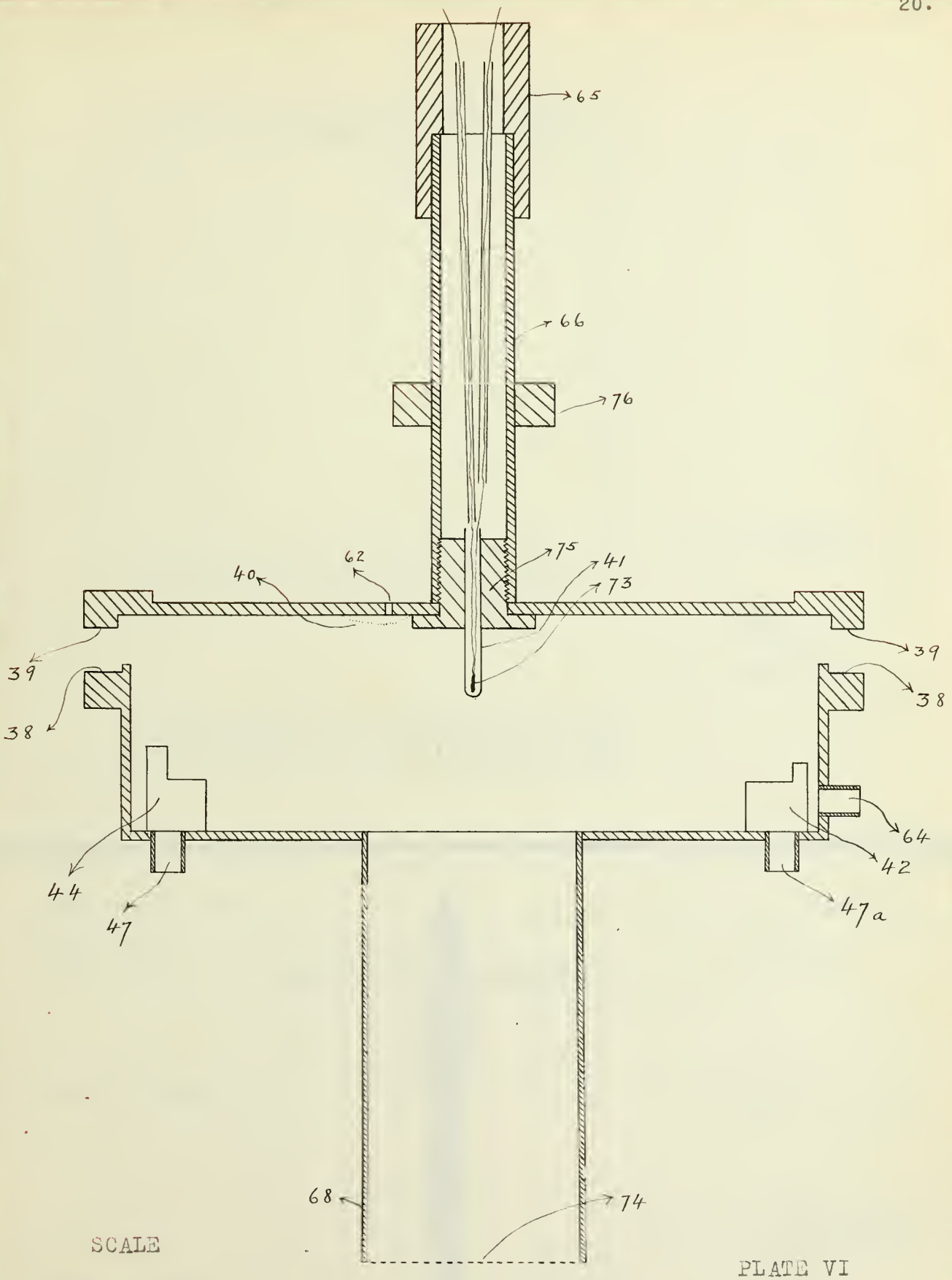
PLATE IV



DIAGRAMMATIC REPRESENTATION OF ELECTRICAL CIRCUITS

PLATE V

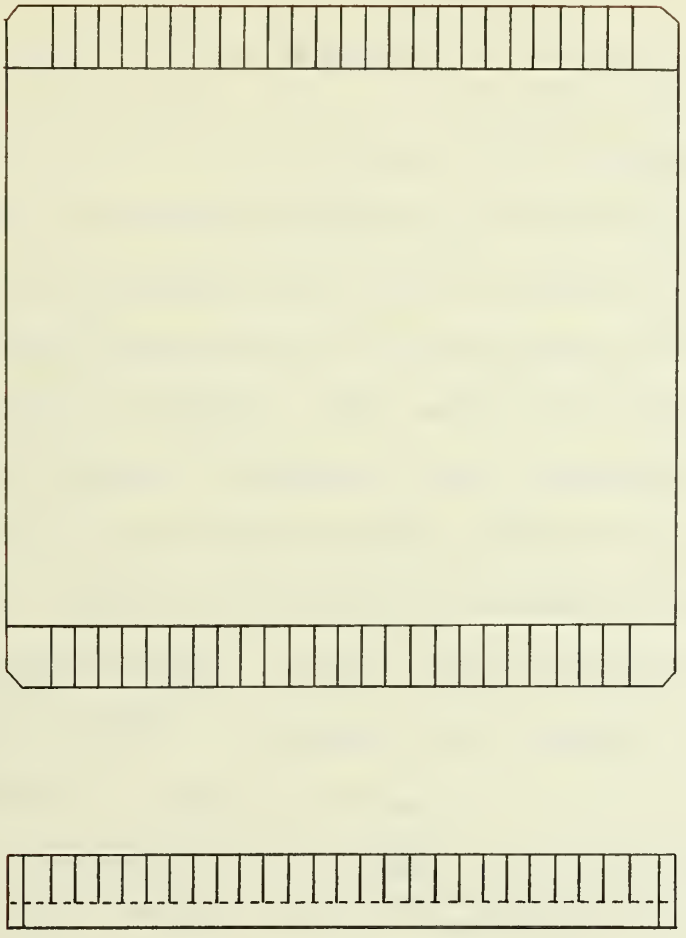


SCALE

FULL SIZE

PLATE VI

"CARBONIZER"



" GRID "

PLATE VII
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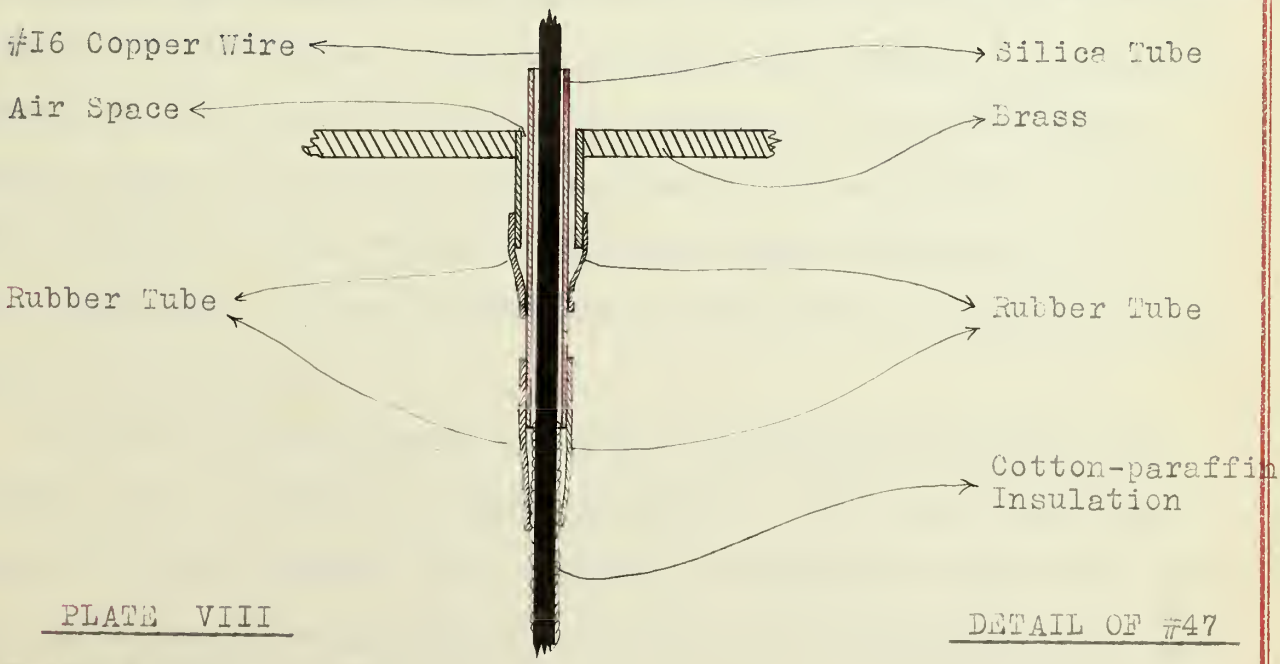

PLATE VIII

DETAIL OF #47

SCALE TWICE ACTUAL SIZE

SECTION 4

THEORY OF MEASUREMENTS AND CALCULATIONS -- PROCEDURE

The electrical heat input could be measured in a number of ways; after considerable testing of various methods, it was finally decided to adopt the method which requires the measurement of (1) the potential drop across the resistor, (2) the current, (3) duration of flow of current, EIt being the energy in joules, where E represents volts, I, amperes and t, seconds. For the potential measurement a Leeds and Northrup, TYPE 7650, potentiometer, $19^{IV,V}$ was used. 20, 21, 22, 23 and G3, PLATES IV and V are accessories to the potentiometer. I and t were measured by means of a water coulometer, $31^{IV,V}$, reported to be correct to $\pm\frac{1}{2}\%$. A coulometer was preferred to other instruments for two reasons: (1) because it is an integrating instrument, a very important consideration, since a more or less constant temperature was maintained in the grid 72^{V} by throwing the switch $13^{IV,V}$ in or out, the coulometer registering only when current was passing and adding up the various elements of It (2) because it gives directly the current-time product, whereas if any other instrument were used for the measurement of current, time would have to be measured with a stopwatch or chronograph, thereby complicating the apparatus and multiplying the errors, especially if time would have to be taken out everytime that current was cut out.

It was at first intended to use a coulometer of greater accuracy, e.g., a silver or copper voltameter, but the current was so large, 12 to 13 amperes, that cathodes of inconveniently large size would have had to be employed, in order not to exceed the low cur-

rent densities which these instruments call for.

The mixed gas, from the coulometer, i.e., the hydrogen and oxygen collected in 27^{IV} and 29^{IV} and measured in 17^{IV}, was calculated to coulombs with the aid of the following expression:

$$\frac{v(b-p)}{T} \times 2.0643 = \text{coulombs}$$

where v is the measured volume, b the barometric pressure, p the vapor pressure of water at the temperature T and T, the absolute temperature at which the gas is measured. (See Lehfeldt, "Electro-Chemistry," pg. 6, Longmans, Green and Co., 1904; the factor there given, 1.8373, is incorrect).

Now, the product coulombs times volts is the number of joules put in. This divided by 4.184 gives the calories put in and this divided in turn by the temperature rise, (Centigrade), gives the water equivalent of the system in grams, i.e. when coke is the material treated. In the case of a run with coal, the heat input as above calculated was used as such and compared with the heat output -- which is the product of temperature rise and water equivalent -- to arrive at the exothermic heat.

To make it possible to multiply the total number of coulombs by volts, it was necessary to keep the potential drop across the grid constant throughtout the experiment, 5 to 6 minutes, for if the voltage varied during the run, it would obviously have been necessary to know how many coulombs corresponded to the respective potential drops. Constancy of potential fall was maintained as follows: 5 or 10 minutes before the heating phase of the experiment, the plate rheostat $16^{IV,V}$ was so adjusted, that the potential drop across the external resistance $34^{IV,V}$, a coil of #18 (B.andS.) nichrome wire, was of such a magnitude--determined by a previous calibration--that it corresponded to a potential drop of 50 volts across the grid 72^{V}

when the rolling contact $25^{IV,V}$ was about in the middle of the slide wire $24^{IV,V}$After this coarse adjustment had been made, fluctuations in the potential drop across the grid were almost entirely eliminated by varying the resistance 24^{V}, which is in series with the grid. The run, as far as the electrical heating phase of the procedure is concerned was then ready to begin, (the grid having previously been loaded and placed in the calorimeter 10^{IV}, as is to be described below). Three observers were required for this phase of the experiment. One manipulated the double-pole, double-throw, knife switch, $13^{IV,V}$and took minute readings on the millivoltmeter 8^{IV}. Another maintained the jacket temperature of the calorimeter 10^{IV} parallel with the temperature of the can and a third manipulated the rolling contact $25^{IV,V}$ along the wire $24^{IV,V}$ in such a manner as to maintain a minimum amount of deflection in the galvanometer $G3^{IV,V}$,(the potentiometer having been set at 50 volts before the start of the experiment). The double-pole, double-throw, knife switch $14^{IV,V}$ was, of course, kept in at the left so that the potentiometer registered potential fall across the grid. $13^{IV,V}$ was kept in until the grid attained a temperature of 500°C and after that the switch was cut out and in, for two minutes, sufficiently often to maintain the temperature in the immediate neighborhood of 500°C. The thermocouple readings do not in any way enter into the calorimetric calculations but serve only to indicate up to what temperature the coal has been carbonized.

To make the arrangement even clearer it should be said that (1) by means of $13^{IV,V}$ current may be fed into either the external resistance $34^{IV,V}$or the grid 72^{V}, the current passing through 16^{V} directly to 34^{V} but through 16^{V} and 24^{V} before it reaches the grid and (2) by means of $14^{IV,V}$ the potentiometer may be used to measure the po-

tential drop across 34 IV,V or the grid, as required.

After the heating has been completed, only one observer is required. The switch 13 IV,V stays out permanently and, outside of measuring the coulometer gas, nothing remains but to get the final temperature of the calorimeter system; this generally took 45 to 55 minutes, during which time, of course, the jacket temperature was constantly equal to that of the can. It should also be noted that during this interval, the residual gas in the carbonizer was cooling, contracting and drawing up water through the gauze 74VI. When the millivoltmeter 8IV registered about 125° C, the string 54II--which protruded through an opening in the cover of the calorimeter 10IV--was pulled. This removed the rubber tip 60II, leaving the end 61II of the coil 67II open to the water of the calorimeter can and allowing (1) the escape of gas (trapped in the carbonizer) through the gauze 40III into the coil 67II, past the point 62II, along the coil and finally out through 61II into the water and (2) the thorough quenching of the grid, etc., which could not otherwise be effectively done. The thermometer 6IV was then read until a constant final temperature was attained, as stated above.

An account of that part of the procedure will now be given which precedes the heating stage above described. 20 to 25 grams of 60 mesh, air-dry coal, weighed to tenth of a gram, were evenly distributed in the grid, the grid having previously been placed in position on the three pegs, 42III 44III in the lower half of the carbonizer and the leads 43III screwed into the binding posts 70I, 71I. A steel spatula was drawn a number of times across the grid in a direction perpendicular to the length of the ribbons; this tended to pack the coal more densely and thereby increased the capacity of the grid. The alberene stone plate, (SEE SECTION 3), was

placed in position and empty spaces in the carbonizer were loosely packed with approximately 12 grams of purified, shredded asbestos, weighed to $\pm\frac{1}{2}$ gram. (In cases where the material did not cake, e.g. the oxygenated coals, (SEE SECTION 6), there was danger of small portions of the powdered coal being blown out of the grid and escaping decomposition. In such cases, special care was taken to produce good contact between the plate and grid by stuffing with asbestos. In spite of these precautions small amounts were occasionally blown out and corrections had to be applied).

The surface $38^{III,VI}$ was greased with vaseline, the rubber gasket (not shown) placed in position, the surface $39^{III,VI}$ greased and the two halves of the carbonizer assembled and clamped as shown in PLATE II. The outer halves of the arms 57^{II}, 58^{II} and the glass tubes 55^{II}, 56^{II} were removed and, after the rubber tip 60^{II}, with the string 54^{II} attached, had been slipped on to the end of the coil 67^{II} at 61^{II} and the junction at 61^{II} coated with paraffin, the carbonizer was placed in the jar 1^{IV}, evacuated twice to 25 millimeters (manometer 3^{IV}) and alternately filled with purified nitrogen from 4^{IV}. The carbonizer was then removed from 1^{IV}, the parts 55, 56, 57 and 58 replaced and the whole put into the calorimeter can (not shown), nitrogen passing into the carbonizer through the tube $46^{II,III}$ while it was being handled in the air.

Enough water was then added so that the can weighed 6700 grams complete, 46^{II} having been disconnected from the nitrogen train and clamped tightly with 45^{II}. The loaded can was placed in the calorimeter 10^{IV}. With the cover of the calorimeter raised about 4 inches, the thermocouple leads 77^{IV}, 78^{IV} and the grid leads

$36^{IV,V}$, $37^{IV,V}$ were drawn through the opening in the cover and screwed into the binding posts 53^{II}, 52^{II}, 51^{II} and 50^{II} respectively. The string 54^{II} was then drawn through the opening to make it accessible from the outside, the cover, thermometers and stirrer placed in position, and the apparatus stirred for one hour to allow the system to come to thermal equilibrium. The initial temperature reading was then taken on the thermometer 6^{IV} and the heating stage, previously described, followed. So much for the actual run.

For a water equivalent determination, the procedure preceding the heating stage was somewhat different. The can was loaded and connected at 50^{II}, 51^{II}, 52^{II} and 53^{II} as above but outside the calorimeter 10^{IV}. The coal was then coked, that is the heating stage was followed through, except that no attention was paid to temperature rise or to getting the system into thermal equilibrium at the start. As soon as heating was over, ice was thrown into the can and nitrogen was passed through the carbonizer, by way of 46^{II}, for about an hour, until the grid had again cooled to room temperature. From then on the apparatus was treated in a manner which coincided exactly with the actual run described above. The difference, then, between the water equivalent determination and the actual run was that the system heated up in the former case was at the start in a condition almost identical with the condition in which the system in the actual run was after the heating had been completed.

After an experiment, the apparatus was disassembled, cleaned, the coke scraped out of the grid and the grid dried over night at 125 - 200° C and, when necessary, gently ignited over a Bunsen

flame.

A leaf from the note book is shown below to indicate how the data were entered and calculated.

RUN # S_1 55b May 5, 1921

Weight of flask coal		83.2	Weight of bag asbestos		93
" " " - coal		59.0	" " " - "		80
" " coal		24.2	" " asbestos		13

Temperature Record

(46" min.)	Final	82.71
	Initial	66.81
	Rise	15.90

Coulometer Record

C.C.	temp.	press.
199.8	22.8	
160.2	22.8	
126.4	22.8	744.9
154.2	22.9	

VOLTAGE 50.00

Room temp. 25° C

Temperature at 5:24 was 72.7° F

Thermocouple Record

Time in minutes	Scale Reading
Start	0.45
1	5.5
2	10.1
3	14.0
3:24	15.5
5:24	
18	3.8
22	0.9
33	0.6
46	0.6

CALCULATIONS

Calibration correction 0.00

Stem exposure " 0.01

RISE (corrected) 15.91 = 8.8390° C.

$$\frac{640.6 \times 724.1 \times 2.0643}{295.8} = 3237 \text{ coulombs}$$

$$\frac{3237 \times 50.00}{4.184} = 38685 \text{ calories INPUT}$$

8.8390 x 4524.4 = 39991 calories OUTPUT

39991 - 38685 = 1306 calories EXOTHERMIC HEAT

SECTION 5

HISTORY, PREPARATION AND ANALYSIS OF SAMPLES

Six samples were worked with in all. As far as possible all material was kept in stoppered bottles under nitrogen to prevent weathering.

SAMPLE #1 was a West Frankfort, Franklin County coal, obtained from Harris, Dillavou and Co., Champaign, Ill. Good $\frac{1}{4}$ pound lumps were picked out of a recent shipment, crushed in a Sturtevant mill to $\frac{1}{4}$ inch size and air dried. The air-dry material was reduced to buckwheat size in a coffee mill and ground on a buckboard to pass a 60 mesh sieve. This material was then used for the experimental work.

SAMPLE #2 was a mixture of $Ba(ClO_3)_2$, anhydrous, 1 part and ignited $BaSO_4$ 10 parts.

SAMPLE #3 -- Vermillion County coal, from the Sharon Coal Co., Urbana, Ill. Good 2 pound lumps were picked from a carload pile, one week old and were treated like SAMPLE #1.

SAMPLE #4 -- Harrisburg, Saline County coal, secured from Huff and Co., Urbana, Ill. Good 2 pound lumps were selected from a bin, which had been stored 2 to 3 weeks. Treatment given was the same as in the case of SAMPLE #1.

SAMPLE #5 -- weathered Franklin County coal. About 220 grams of air-dry SAMPLE #1, buckwheat size, were placed in an air-drying oven kept at about 35° C. After 6 weeks the coal had lost in weight 2.3 grams and still gave a fairly good coke in a crucible test. It was therfore ground to 60 mesh, placed in oven at 105° and raked once a day so as to expose fresh surfaces to the air. After 10

days' heating, it had lost only 0.5 grams, whereas according to the moisture determination (SEE TABLE II, below), it should have lost 3.64%. Taking into account the 2.3 grams lost during the 6 weeks' exposure, it seems that the coal absorbed at 105°C about 2.5% of oxygen -- possibly also CO_2 and N_2 -- from the air. This oxygenated material was submitted to tests in the carbonizer.

SAMPLE #6 -- weathered Vermillion County coal. In this case a part of 60 mesh, air-dry SAMPLE #3 was placed directly in the oven kept at 105°. A more careful record of weights was kept and is recorded below.

TABLE I

SHOWING ABSORPTION OF OXYGEN BY VERMILLION COUNTY COAL AT 105°C

DURATION OF HEATING HOURS	WEIGHT OF COAL GRAMS
Start	269.7
2	254.4
12	255.5
24	256.5
38	256.8
60	256.8
84	257.6
108	259.1
132	599.6
154	260.1
176	260.6
204	260.6
228	260.8

According to the moisture determination, (SEE TABLE II), the sample should have lost 16.02 grams at 105° and since it lost only 8.9, the absorption from the air amounts to 7.12 grams or 2.64%. This is based on the assumption that the coal lost no more weight during ten days' heating, either as hygroscopic moisture or by oxidation of hydrogen, than it lost on one hour's heating at 105°

in a CO_2 atmosphere, the conditions under which moisture loss was determined. Since that is undoubtedly not the case, the 2.64% is only a minimum, the amount of material actually absorbed being very probably higher. The same criticism is applicable to the calculation made for SAMPLE #5.

The loss on air-drying was as follows: SAMPLE #1, 5.19%; #3, 10.48%; #4, 3.5%.

Table II gives the proximate and ultimate analyses of the samples. All determinations were made in duplicate; single figures indicate calculated percentages.

TABLE II

ANALYSES OF SAMPLES

SAMPLE NO.	MOISTURE	VOLATILE MATTER	FIXED CARBON	ASH	C	H	O	N	S	CALS. PER GRAM	BASIS
1	3.67	36.21	52.54	7.72	71.61	4.97	9.01	1.57	1.26	7156	
	3.61	36.07		7.63	72.18			1.51	1.29	7166	
3	5.98	37.26	49.48	7.43	69.82	4.84	9.20	1.83	1.07	6833	AIR-DRY
	5.89	36.95		7.49	69.57			1.79	1.03	6821	
4	2.53	35.16	53.03	9.41	70.64	5.01	8.54	1.85	2.00	7122	
	2.46	35.00		9.37	70.73			1.98	1.90	7104	
1	....	37.50	54.52	7.96	74.61	5.16	9.35	1.60	1.32	7431	
3	....	39.45	52.60	7.93	74.09	5.15	9.78	1.92	1.12	7258	MOISTURE FREE
4	....	35.97	54.38	9.63	72.48	5.14	8.76	1.96	2.00	7294	

The analyses cannot be expected to be typical of these coals, inasmuch as the samples were selected and not representative.

SECTION 6

EXPERIMENTAL DATA -- DISCUSSION

It was thought desirable to submit the accuracy of the method to an absolute test by charging the grid with material which was known to yield a definite quantity of exothermic heat. A suitable substance was not easy to find for it had to fulfill a variety of requirements, some of which were:

1. Sharp decomposition at a temperature not much above 500°C.
2. Decomposition should be complete in 5 or 6 minutes.
3. No complicating side reactions should occur.
4. The substance should not melt, for if it did, it would run out of the grid.
5. The products of decomposition should preferably be solids insoluble in water, etc., etc.

$Ba(Cl\ O_3)_2$ diluted with $Ba\ SO_4$ was finally decided upon. The reaction

$$2\ Ba(Cl\ O_3)_2 = Ba(ClO_4)_2 + BaCl_2 + 2O_2$$

proceeding rather sharply at 425 C° with a liberation of 92 calories per gram of $Ba(ClO_3)_2$. A few experiments were made but the work had to be discontinued on account of the corrosive action, at 450°C, of the oxygen and a small amount of chlorine which also formed. Owing to these circumstances, the results were not sufficiently reliable. However, such indications as were obtained, seemed to lead to the conclusion, that the accuracy was probably not better than ±20% or 25%. This agrees fairly well with the estimation of the accuracy, made in SECTION 2, on purely hypothetical grounds.

TABLE III, below, gives the exothermic values of the five

coals studied in this investigation. The quantities recorded are means of 4 determinations, with the average deviation from the mean in the extreme right hand column.

TABLE III

EXOTHERMIC HEAT VALUES FOR FIVE COALS

SAMPLE NO.	NAME	EXOTHERMIC HEAT IN CALORIES PER GRAM		A. D. IN %
		AIR-DRY COAL	MOISTURE FREE COAL	
1	Franklin	26	27	22
3	Vermillion	39	41	8.5
4	Saline	13	13	16
5	#1 Weathered	55	57	6.3
6	#3 Weathered	58	62	13

In the case of SAMPLE #4, the material was only raised to 500° and the heating was stopped, i.e. the 2 minute period, (SEE SECTION 4, infra), had to be dispensed with because of the difficulty experienced in maintaining at 500° a constant potential drop across the grid. This, however, should not materially affect the result, since very little decomposition -- as indicated by gas evolution -- occurred at 500° as compared with the amount of decomposition up to 500° C.

DISCUSSION

It is evident from the results that the exothermic heat increases with oxygen content, both with the oxygen normally present and with the oxygen taken up on weathering, especially when the coals are compared on the moisture free basis, which is quite ap-

propriate, considering that the material must necessarily be free of its moisture at the more or less elevated decomposition temperatures. For the three coals studied, the exothermic heat, on the moisture free basis, is given roughly by the expression

$$12.5 + 28(n - 8.75)$$

where n is the per cent of oxygen on the moisture free basis and the other terms are empirical constants. The oxygen taken up on weathering obviously yields much greater quantities of exothermic heat than the oxygen of composition, the ratios for 1% of oxygen being: for Franklin County coal, 12 to 3, for Vermillion County coal, 8 to 4 calories.

It is interesting to note that though the Franklin and Vermillion County coals are rather far apart in exothermicity, the weathered coals corresponding to them come very much closer to being the same.

The ratio of exothermic heat to per cent oxygen on the "unit coal" basis is interesting, at least for the oxygenated coals.

TABLE IV

RATIO OF EXOTHERMIC HEAT TO PERCENT OXYGEN

"UNIT COAL" BASIS

SAMPLE NO.	NAME	EXOTHERMIC HEAT IN CALORIES	% O	CALS. / % O
1	Franklin	31	10.3	3.01
3	Vermillion	46	10.8	4.26
4	Saline	15	10.1	1.48
5	#1, Weathered	63	13.2	4.77
6	# 3, Weathered	68	13.9	4.88

Here, again, the ratios for #1 and #3 are rather far apart, whereas for #5 and #6, the corresponding oxygenated coals, the ratios are remarkably close.

Heretofore, it has been customary to compare exothermic heats as per cents of the calorific values of the coals. It is difficult to see what importance such a ratio can have. It seems that it would be more instructive to know what part of the heat actually required to coke the coal is furnished by the exothermic reaction. By the "heat actually required to coke the coal" is meant the sum of the various quantities used up in vaporizing the liquid products of carbonization and the combined heat capacities of all the products. Such a definition is not purely arbitrary. It has a real significance in the low-temperature carbonization process; for, the coal is brought up to a suitable reaction temperature, i.e., a temperature at which a vigorously exothermic stage sets in and from then on, only such a quantity of heat is fed in through the walls of the retort as is necessary to compensate for the loss due to radiation, conduction and heat carried out by volatile products. The actual energy of carbonization, as stated in SECTION 1, is furnished primarily by the exothermic heat of the reaction.

Fortunately, the data taken in connection with SAMPLES 3 and 5, the Vermillion coals, make it possible to estimate the ratio of the exothermic heat to the heat actually consumed in carbonizing the coal. At first hand, it may appear that the difference between the heat input in an actual run and the heat input in a corresponding water equivalent determination should represent the heat actually required to carbonize the coal. This would be true if no heat were lost by radiation and conduction. This loss, which must

be subtracted from the difference referred to above, may be estimated from the temperature rise, indicated on thermometer 6^{IV}, at the time when the heating period was ended. In the case of SAMPLES 3 and 4, this observation was made, in addition to the observations mentioned in SECTION 4. Now the ratio of the temperature rise, up to the end of the heating period, to the total rise is a measure of the heat lost by radiation and conduction, the amount by which the difference in the heat inputs for coke and coal must be diminished to arrive at the quantity of heat actually required to decompose the coal. TABLE V gives all the necessary data and calculations. In this case, too, the values are averages of several determinations.

TABLE V

SHOWING RATIO OF EXOTHERMIC HEAT TO THE HEAT "ACTUALLY REQUIRED TO DECOMPOSE THE COAL."

SAMPLE NO.	AVERAGEHHEAT INPUT IN CALORIES		DIFFERENCE		TEMPERATURE RISE ° F		HEAT IN CALS. PER GRAM		RATIO
	COKE	COAL	TOTAL	PER GRAM	TOTAL	AT END OF HEAT. PERIOD	OF DE-COMPO-SITION	EXO-THER-MIC	
3	31180	36290	5110	265	14.37	6.50	113	39	35%
5	34550	37580	3030	130	15.26	5.64	82	55	67%

In the case of #3, the heat "actually required to decompose the coal" also includes a correction for the heat of vaporization of its moisture, i.e. the moisture lost at 105°, for that cannot in any sense be considered a product of decomposition.

The samples listed above are, of course, relatively strongly exothermic and less exothermic coals would no doubt show a smaller

ratio. Still, the figures do show that the exothermic heat is not an inconsiderable factor in the energy required to decompose the coal.

Perhaps the most significant point to be noted is that the exothermic values here reported are very much lower than those that are to be found in the literature. Taking the highest value obtained, 39 calories (SAMPLE #3) and increasing it by 50%, to correct for a possible though highly improbable error, the exothermic heat is still only 0.9% of the calorific value, whereas the values in the literature range from 2 to 7%, as stated in SECTION #1. The most likely explanation for this difference is that the results here given represent exothermic heat up to 500° C. only, while the high results mentioned were obtained in high temperature carbonizations. Evidence for the existence of marked exothermic reactions above 500° is not lacking. The heating curves furnished by the work of Vliet (unpublished report) and Hollings and Cobb[1] give unmistakable proof that considerable evolution of heat occurs between 600° and 800° C.

SECTION 7

SUMMARY

1. A new method has been developed for the study of the thermal behavior of coals during carbonization.

2. The method affords semi-quantitative results with an accuracy probably not better than ±25%.

3. The exothermicity of high oxygen coals has been demonstrated by this new method.

4. The exothermic heat of carbonization of three Illinois coals and two weathered Illinois coals has been measured.

5. It has been confirmed that exothermicity increases with oxygen content.

6. It has been established, for the first time, that the oxygen absorbed during weathering contributes from 2 to 4 times as much heat, per unit of oxygen, as the oxygen originally in the coal.

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SECTION 9

APPENDIX

In compiling the table which follows, an attempt was made to recalculate the data more or less to the same basis throughout but in many cases that was not possible owing to the failure of the authors to state explicitly what the figures were or how they were arrived at. So that, although the "heat losses," (SEE SECTION 2, for a definition of this term), are not strictly comparable, they do serve at least to show the general order of magnitude.

It would, of course, be interesting to compare ultimate compositions, especially oxygen contents, with the respective exothermic heats but the ultimate analyses are not available in a sufficient number of cases. It is, however, true that exothermicity increases with oxygen content.

A number of values for wood is included for purposes of comparison.

The first figure in the table was found by a calculation based on statements made in Lewes', "Carbonization of Coal" page 90, Benn Bros., Ltd., London 1918.

COMPILATION OF EXOTHERMIC HEAT VALUES FROM THE LITERATURE

Name of Coal	Fixed Carbon %	Ash %	H_2O %	Heat of Combustion Cals. per Gram	"Heat Loss" % of Calorific Value	Index No. to Bibliography
. . . . .	.....	....	....	....	0.9	8
. . . . .	.....	....	....	....	6.6	9
Commentry	.....	....	....	....	3.5	10
Belgian Anthracite	86.75	3.75	1.23	8217	4.8	11
Ruhrmagerkohle	81.92	4.18	1.19	8124	5.67	11
Ruhresskohle	81.26	3.96	0.97	8202	4.93	11
Ruhrfettkohle I	79.56	2.64	0.77	8427	5.10	11
Ruhrfettkohle II	74.63	3.17	1.02	8279	3.01	11
Ruhrgassflammkohle	62.72	6.42	1.57	7686	5.76	11
Bright Coal Nottinghamshire	49.23	3.06	9.60	7004	4.6	12
Trencherbone Coal Lancashire	57.64	1.42	2.58	8066	3.8	12
Kinneil Coal	57.61	4.11	7.50	7811	4.1	12
Low Main Seam Durham	61.74	1.91	2.36	8250	4.5	12
Hutton Seam Durham	65.60	0.94	1.61	8594	3.3	12
Barnsely Coal Yorkshire	59.09	8.65	0.94	7276	2.6	12
Durham Ballarat Seam	70.71	2.95	2.81	8321	3.9	12
Nixons Navigation Coal, Wales	77.20	1.79	0.98	8486	3.0	12
Best Hard Coal Nottinghamshire	53.84	3.36	7.50	7208	4.2	12
. . . . .	.....	....	....	....	3.06	13
. . . . .	.....	....	....	....	3.1	13
Gardanne	39.8	10.79	10.55	5673	7.20	14
Chapelle sous Dun	42.2	14.39	10.43	5876	4.4	14
Pyranaenkohle	52.4	4.75	3.88	7156	6.68	14

Name of Coal	Fixed Carbon %	Ash %	H_2O%	Heat of Combustion Cals. per Gram	"Heat Loss" % of Calorific Value	Index No. to Bibliography
Bruay	58.1	3.96	2.36	7663	6.0	14
Blanze	51.7	13.70	2.93	6793	4.8	14
St. Etienne	64.9	5.50	0.94	8085	3.3	14
Lens	67.3	4.66	0.98	8138	3.7	14
Ronchamp	63.8	14.05	0.87	7369	4.5	14
Grand'Combe	69.3	10.53	0.74	7531	2.6	14
Meurchin	84.3	2.93	1.08	8326	2.2	14
Epinac	77.8	11.05	0.97	7505	4.4	14
Ostricourt	85.0	4.71	1.10	8115	3.2	14
La Mure	89.2	3.41	3.48	7627	3.6	14
. . . . .	.....	....	....	....	3.4	15
Wood	.....	....	....	....	6.3	16
"	.....	....	....	....	4.6	16
"	.....	....	....	....	5.9	16
"	.....	....	....	....	6.6	16
Purified Cellulose	.....	....	....	....	3.8	16
" "	.....	....	....	....	5.4	16
" "	.....	....	....	....	5.3	16
" "	.....	....	....	....	6.4	16
Wood	.....	....	....	....	3.5	17
"	.....	....	....	....	2.0	17
"	.....	....	....	....	-1.0	17
"	.....	....	....	....	10-15	4

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